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(54) Title: ACYLOXY SILANE TREATMENTS FOR METALS

(57) Abstract: A method of treating a metal surface by application of a solution containing at least one acyloxy silane and at least one basic compound. A composition having at least one acyloxy silane and at least one basic compound is also provided, along with a silane coated metal surface.



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ACYLOXY SILANE TREATMENTS FOR METALS

Background of the Invention

Field of the Invention

5 The present invention relates to silane coatings for metals. More particularly, the present invention provides coatings which include an acyloxy silane, and are particularly useful for preventing corrosion and/or promoting
10 adhesion between a metal substrate and a polymer layer applied to the treated metal substrate. Solutions for applying such coatings, compositions as well as methods of treating metal surfaces, are also provided.

Description of Related Art

15 Most metals are susceptible to corrosion, including the formation of various types of rust. Such corrosion will significantly affect the quality of such metals, as well as that of the products produced therefrom. Although rust and the like may often be removed, such steps are costly and may further diminish the strength of the metal. In addition, when polymer coatings such as paints, adhesives or rubbers are applied to the metals, corrosion may cause a loss of
20 adhesion between the polymer coating and the metal.

 By way of example, metallic coated steel sheet such as galvanized steel is used in many industries, including the automotive, construction and appliance industries. In most cases, the galvanized steel is painted or otherwise coated with a polymer layer to achieve a durable and aesthetically-pleasing product.
25 Galvanized steel, particularly hot-dipped galvanized steel, however, often develops "white rust" during storage and shipment.

 White rust (also called "wet-storage stain") is typically caused by moisture condensation on the surface of galvanized steel which reacts with the zinc coating. On products such as GALVALUME®, the wet-storage stain is black in
30 color ("black rust"). White rust (as well as black rust) is aesthetically unappealing and impairs the ability of the galvanized steel to be painted or

otherwise coated with a polymer. Thus, prior to such coating, the surface of the galvanized steel must be pretreated in order to remove the white rust and prevent its reformation beneath the polymer layer. Various methods are currently employed to not only prevent the formation of white rust during shipment and storage, but also to prevent the formation of white rust beneath a polymer coating (e.g., paint).

In order to prevent white rust on hot-dipped galvanized steel during storage and shipping, the surface of the steel is often passivated by forming a thin chromate film on the surface of the steel. While such chromate coatings do provide resistance to the formation of white rust, chromium is highly toxic and environmentally undesirable. It is also known to employ a phosphate conversion coating in conjunction with a chromate rinse in order to improve paint adherence and provide corrosion protection. It is believed that the chromate rinse covers the pores in the phosphate coating, thereby improving the corrosion resistance and adhesion performance. Once again, however, it is highly desirable to eliminate the use of chromate altogether. Unfortunately, however, the phosphate conversion coating is generally not very effective without the chromate rinse.

Recently, various techniques for eliminating the use of chromate have been proposed. These include coating the galvanized steel with an inorganic silicate followed by treating the silicate coating with an organofunctional silane (U.S. Patent No. 5,108,793).

U.S. Patent No. 5,292,549 teaches the rinsing of metallic coated steel sheet with a solution containing an organofunctional silane and a crosslinking agent.

U.S. Patent No. 6,071,566 relates to a method of treating a metal substrate to provide permanent corrosion resistance. The method comprises applying a solution containing one or more vinyl silanes in admixture with one or more multi-silyl-functional silanes to a metal substrate in order to form a coating.

Various other techniques for preventing the formation of white rust on galvanized steel, as well as preventing corrosion on other types of metals, have also been proposed. Many of the proposed techniques described in the prior art are, however, ineffective, or require time-consuming, energy-inefficient, multi-step processes. Thus, there is a need for a simple, low-cost technique for preventing corrosion on the surface of metal.

A particular problem associated with the silane treatments of the prior art is the rate of hydrolysis of the silane compounds. Such compounds are generally hydrolysed in water, at a specific pH, prior to application of the solution to the substrate to be treated. The rate of hydrolysis varies between silanes, and the degree of hydrolysis is a priori not known. Generally, it has to be guessed when the solution is ready for application. When the solution has turned cloudy, this indicates that condensation of the silanes has occurred and the effectiveness of the treatment solution is reduced.

A further problem with the prior art techniques is the inherent insolubility in aqueous media of some of the silanes employed in the metal treatments. To overcome this problem it is commonplace to dissolve the silane with the aid of an organic solvent, for example, alcohols. Thus a final treatment solution commonly contains up to 60% alcohol. The use of many volatile organic compounds (VOCs), including solvents, is highly undesirable from an economic, as well as an environmental perspective. Apart from the cost of such organic solvents, including the cost of their disposal and methods of treatment solution preparation, such compounds present a threat to the environment and are a hazard to the premises and personnel handling the materials.

A further problem is that the silane systems used in treatment solutions have to have their pH maintained in specific ranges by the initial and continuous addition of acids or bases.

It would therefore be desirable to provide an effective treatment method for metal surfaces, especially to prevent corrosion, and/or improve adhesion.

It would also be desirable to provide a treatment solution useful in preventing corrosion, and/or adhesion promotion of metal surfaces, for example,

steel, aluminium, aluminium alloys, zinc, zinc alloys, magnesium, magnesium alloys, copper, copper alloys, tin and tin alloys, particularly zinc, zinc alloys, and other metals having a zinc-containing coating thereon

It would additionally be desirable to provide a metal surface having improved corrosion resistance and/or improved adhesion characteristics.

Summary of the Invention

The present invention provides a method of treating a metal surface, comprising the steps of:

- (a) providing a metal substrate; and
- (b) applying a solution to said metal substrate, said solution comprising
 - (i) at least one acyloxy silane which comprises at least one acyloxy group, wherein said silane has been at least partially hydrolysed; and
 - (ii) at least one basic compound;

wherein the acyloxy silane and the basic compound are present in concentrations to provide a solution pH of between about 3 and about 10, more preferably between about 4 and about 8, most preferably 4 to 5 and wherein the solution is substantially free of acid other than acid produced upon hydrolysis of the acyloxy silane.

The present invention also provides a composition comprising at least one acyloxy silane and at least one basic compound, wherein the at least one acyloxy silane is at least partially hydrolyzed. A metal surface having improved corrosion resistance and/or adhesion and a composition concentrate is also provided.

Detailed Description of the Invention

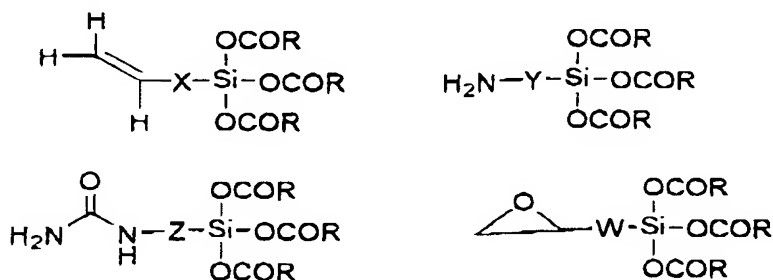
The acyloxy silane(s) utilised in the present invention may comprise one or more silyl groups and the solution may contain a mixture of acyloxy silanes

Where the acyloxy silane comprises a single silyl group the silicon atom is tetrasubstituted, wherein the substituents are individually selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, alkaryl, aralkyl, vinyl, amino, ureido, glycidoxy, epoxy, hydroxy, alkoxy, aryloxy and acyloxy, or any of the group alkyl, alkenyl, alkynyl, aryl, alkaryl and aralkyl substituted by a group selected from the group consisting of vinyl, amine, ureido, glycidoxy, epoxy, hydroxy and alkoxy, with the proviso that at least one of the substituents on the silicon atom is an acyloxy group.

Where more than one acyloxy group is attached to the silicon atom of the silyl group, the acyloxy groups are preferably all the same. The acyloxy group(s) are preferably selected from the group consisting of C₂₋₁₂ alkanoyloxy, C₃₋₁₂ alkenoyloxy, C₃₋₁₂ alkynoyloxy and C₇₋₁₈ arenoyloxy, preferably C₂₋₆ alkanoyloxy, C₃₋₆ alkenoyloxy, C₃₋₆ alkynoyloxy and C₇₋₁₂ arenoyloxy. Most preferably the acyloxy groups are all the same and are ethanoyloxy (acetoxyl) or methanoyloxy groups.

Where the acyloxy silane comprises a single silyl group, preferably three of the substituents on the silyl group are acyloxy groups and the fourth substituent is preferably selected from a the group consisting of vinyl or vinyl substituted group, amine or amine substituted group, ureido or ureido substituted group and glycidoxy or glycidoxy substituted group.

In a particularly preferred embodiment, the acyloxy silane is selected from the group consisting of



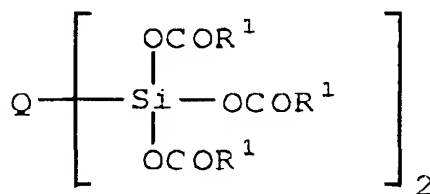
wherein W, X, Y and Z are selected from the group consisting of a C-Si bond, substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups and unsubstituted aromatic groups; and

R is selected from methyl, ethyl and propyl, preferably ethyl.

The acyloxy silane may comprises more than one silyl group. Although the term acyloxy silane generically refers to such a compound, it may be referred to as a multi-silyl-acyloxy silane. More than one multi-silyl-acyloxy silane may be employed in a mixture with one or more other multi-silyl-acyloxy silanes or one or more acyloxy silanes containing a single silyl group as described above.

The acyloxy groups bound to the silicon atoms of the silyl groups of the multi-silyl-acyloxy silane are preferably all the same and are preferably selected from the group consisting of C₂₋₁₂ alkanoyloxy, C₃₋₁₂ alkenoyloxy, C₃₋₁₂ alkynoyloxy and C₇₋₁₈ arenoyloxy, preferably C₂₋₆ alkanoyloxy, C₃₋₆ alkenoyloxy, C₃₋₆ alkynoyloxy and C₇₋₁₂ arenoyloxy. Most preferably the acyloxy groups are all the same and are ethanoyloxy or methanoyloxy groups.

Preferably the multi-silyl-acyloxy silane utilised in the present invention has the structure



wherein Q is selected from the group consisting of either a bond, an aliphatic or aromatic group; and

R¹ is selected from methyl, ethyl and propyl.

Preferably Q is selected from the group consisting of a bond, C₁-C₆ alkylene, C₂-C₆ alkenylene, C₁-C₆ alkylene substituted with at least one amino group, C₂-C₆ alkenylene substituted with at least one amino group, C₁-C₆ alkylene substituted with at least one sulfide group containing 1 to 6 sulfur atoms, C₂-C₆ alkenylene substituted with at least one sulfide group containing 1 to 6 sulfur atoms, arylene and alkylarylene. In the case where Q is a bond, the

multi-functional silane comprises two trisubstituted silyl groups which are bonded directly to one another. Preferred multi-silyl-acyloxy silane are bis-(triacetoxysilyl)alkane, bis-(triacetoxysilylalkyl)amine and bis-(triacetoxysilylalkyl)tetrasulfide, most preferably bis-(triacetoxysilyl)ethane, 5 bis-(triacetoxysilylpropyl)amine and bis-(triacetoxysilylpropyl)tetrasulfide.

In an especially preferred embodiment, the acyloxy silane utilised in the present invention is vinyltriacetoxysilane.

Acyloxy silanes utilised in the present invention generally dissolve and hydrolyze readily and completely in water to produce organic acids. For 10 example, where an acetoxy silane is used, acetic acid is produced. Unlike the analogous alkoxy silanes commonly utilised in the prior art which produce alcohols upon hydrolysis, the acyloxy silanes utilised in the present invention produce substantially none or small amounts of VOCs depending on the level of non-acyloxy group substitution in the silanes.

Depending on the level of substitution of acyloxy groups in the silanes 15 utilised in the present invention, the pH of the resultant solution can be predetermined and manipulated. Commonly, high degrees of acyloxy group substitution are present, for example $\approx 100\%$ substitution, and this can result in a pH as low as 1 or 2. At these low levels of pH, the hydrolysed acyloxysilanes 20 tend to condense, therefore reducing their efficacy. It is therefore necessary to add a base to maintain the pH in an optimal range.

Preferably, where a single silyl group-containing silane is used as the acyloxy silane, 3 of the groups attached to the silicon atom of the silyl group are acyloxy groups, preferably methanoyloxy or acetoxy.

25 Preferably, where a multi-silyl-acyloxy silane is used, 3 of the groups attached to the each silicon atom of each silyl group are acyloxy groups, preferably methanoyloxy or acetoxy.

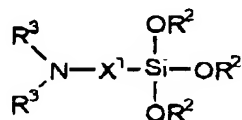
The pH of the silane mixture is between about 3 and about 10, more preferably between about 4 and about 8, most preferably 4 to 5 and should be 30 maintained. The pH may be adjusted by the addition of one or more basic compounds or addition of acyloxy silane(s).

During preparation of the treatment solution, a pH of above 2, more preferably above 3, most preferably between 4 and 5 should be maintained.

In order to maintain an optimal pH during preparation of the treatment solution, a basic compound is applied to the treatment solution. The identity of the basic compound(s) is not critical but it is highly beneficial to provide a compound which complements the acyloxy silane. "Complements" means that the basic compound aids, or at least does not substantially detract from the formation of the silane coating on the metal substrate or from the coatings effectiveness in improving corrosion resistance and/or adhesion promotion.

To maintain the pH in the preferred range, the acyloxy silane and the basic compound are preferably mixed together prior to the addition of water and subsequently dissolved in water. Exemplary basic compounds include the carbonates, hydrogen carbonates and hydroxides of the alkali and alkaline earth metals, organic amines, ammonia, amides and the like. A mixture of different basic compounds may be added to the treatment composition.

In a preferred embodiment, the basic compound is a basic silane compound. For example, amino silanes are particularly preferred. In one embodiment, amino silanes which may be employed in the present invention each have a single trisubstituted silyl group in addition to the basic amine moiety, wherein at least one of the substituents is an alkoxy group. Thus, the amino silanes which may be used in the present invention have the general structure



R^2 is chosen from the group consisting of hydrogen and C_1 - C_{24} alkyl, preferably C_1 - C_6 alkyl and each R^2 may be the same or different. Preferably R^2 is individually chosen from the group consisting of hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl and ter-butyl.

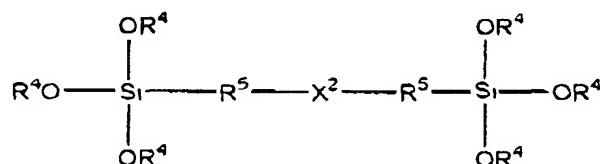
X¹ is a group selected from the group consisting of a bond, a substituted or unsubstituted aliphatic or aromatic group. Preferably X¹ is selected from the group consisting of a bond, C₁-C₆ alkylene, C₂-C₆ alkenylene, C₁-C₆ alkylene substituted with at least one amino group, C₂-C₆ alkenylene substituted with at least one amino group, C₆₋₁₈ arylene and C₇-C₁₈ alkylarylene;

R³ is a group individually selected from the group consisting of hydrogen, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₆ alkyl substituted with at least one amino group, C₂-C₆ alkenyl substituted with at least one amino group, arylene and alkylarylene.

Preferably R³ is individually selected from the group consisting of hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl, ter-butyl and acetyl.

Particular preferred amino silanes employed in the method of the present invention are γ-aminopropyltriethoxysilane and γ-aminopropyl trimethoxysilane.

In another embodiment, the amino silane may be a bis-silyl aminosilane(s). Such a compound comprises an aminosilane having two trisubstituted silyl groups, wherein the substituents are individually selected from the group consisting of hydroxy and alkoxy. Preferably, the bis-silyl aminosilane comprises:



wherein each R⁴ is individually selected from the group consisting of: hydrogen and C₁ - C₂₄ alkyl;

each R⁵ is individually selected from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups; and

X² is either:

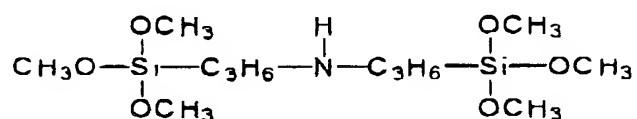


wherein each R⁶ is individually selected from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

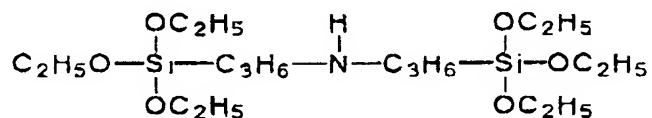
R⁷ is selected from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups

Particularly preferred bis-silyl aminosilanes which may be used in the present invention include:

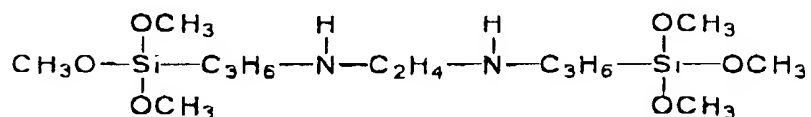
bis-(trimethoxysilylpropyl)amine (which is sold under the tradename A-1170 by Witco):



bis-(triethoxysilylpropyl)amine:



and *bis*-(triethoxysilylpropyl)ethylene diamine:



Particularly preferred combinations of acyloxy silanes and basic compounds are:
 vinyltriacetoxysilane and *bis*-(trimethoxysilylpropyl)amine;
 1,2-*bis*-(triethoxysilyl)ethane and *bis*-(trimethoxysilylpropyl)amine;
 vinyltriacetoxysilane and aminopropyltriethoxysilane;
 vinyltriacetoxysilane and *bis*-(triethoxysilylpropyl)amine;
 1,2-*bis*-(triethoxysilyl)ethane and *bis*-(triethoxysilylpropyl)amine;
 vinyltriacetoxysilane and aminopropyltrimethoxysilane.

Where basic silanes are used as the basic compound, additional basic compounds may be used, for example, the inorganic bases referred to above.

The solutions and methods of the present invention may be used on a variety of metals, including steel, aluminium, aluminium alloys, zinc, zinc alloys, magnesium, magnesium alloys, copper, copper alloys, tin and tin alloys. In particular, the present method is particularly useful on zinc, zinc alloy, and metals having a zinc-containing coating thereon, as well as aluminium or aluminium containing substrates. For example, the treatment solutions and methods of the present invention are useful in preventing corrosion of steel having a zinc-containing coating, such as: galvanized steel (especially not dipped galvanized steel), GALVALUME® (a 55%-Al/43.4%-Zn/1.6% - Si alloy coated sheet steel manufactured and sold, for example, by Bethlehem Steel Corp), GALFAN® (a 5%-Al/95%-Zn alloy coated sheet steel manufactured and sold by Weirton Steel Corp., of Weirton, WV), galvaneal (annealed hot dipped galvanized steel) and similar types of coated steel. Zinc and zinc alloys are also particularly amenable to application of the treatment solutions and methods of the present invention. Exemplary zinc and zinc alloy materials include: titanium-zinc (zinc which has a very small amount of titanium added thereto), zinc-nickel alloy (typically about 5% to about 13% nickel content), and zinc-cobalt alloy (typically about 1% cobalt).

The solutions of the present invention may be applied to the metal prior to shipment to the end-user, and provide corrosion protection during shipment and storage (including the prevention of wet-storage stain such as white rust). If a paint or other polymer coating is desired, the end user may merely apply the paint or polymer (e.g., such as adhesives, plastics, or rubber coatings) directly on top of the silane coating provided by the present invention. The silane coatings of the present invention not only provide excellent corrosion protection even without paint, but also provide superior adhesion of paint, rubber or other polymer layers. Thus, unlike many of the currently-employed treatment techniques, the silane coatings of the present invention need not be removed prior to painting (or applying other types of polymer coatings such as rubber).

Suitable polymer coatings include various types of paints, adhesives (such as epoxy automotive adhesives), and peroxide-cured rubbers (e.g., peroxide-cured natural, NBR, SBR, nitrile or silicone rubbers). Suitable paints include polyesters, polyurethanes and epoxy-based paints. Plastic coatings are also suitable including acrylic, polyester, polyurethane, polyethylene, polyimide, polyphenylene oxide, polycarbonate, polyamide, epoxy, phenolic, acrylonitrile-butadiene-styrene, and acetal plastics. Thus, not only do the coatings of the present invention prevent corrosion, they may also be employed as primers and/or adhesive coatings for other polymer layers.

The solutions of the present invention do not require the use or addition of silicates.

The compositions may optionally comprise other silane compounds to the acyloxy silanes or the basic silanes disclosed herein.

The treatment solution is aqueous, and may optionally include one or more compatible solvents (such as ethanol, methanol, propanol or isopropanol) although their presence is not normally required. Where an organic solvent is required, ethanol is preferred. Preferably, solutions of the present invention are substantially free of organic solvents and VOCs.

As mentioned above, the silane(s) in the solution of the present invention are at least partially, and preferably are substantially fully hydrolyzed in order to facilitate the bonding of the silanes to the metal surface and to each other. During hydrolysis, the alkoxy groups in the case of the non-acyloxy silanes and the acyloxy in the case of the acyloxy silanes are replaced by hydroxyl groups. Hydrolysis of the silanes may be accomplished, for example, by merely mixing the silanes in water, and optionally including a solvent (such as an alcohol) in order to improve silane solubility and solution stability.

In order to accelerate silane hydrolysis and avoid silane condensation during hydrolysis, the pH may be maintained below about 8, more preferably between about 4 and about 6, and even more preferably between about 4 and about 5.

It should be noted that the various silane concentrations discussed and claimed herein are all defined in terms of the ratio between the amount (by volume) of unhydrolyzed silane(s) employed to prepare the treatment solution (i.e., prior to hydrolyzation), and the total volume of treatment solution components (i.e., acyloxy silanes, basic compound, water, and optional solvents. In the case of acyloxy silane(s), the concentrations herein (unless otherwise specified) refer to the total amount of unhydrolyzed acyloxy silanes employed, since multiple acyloxy silanes may optionally be present. The basic compounds concentrations herein are defined in the same manner.

As for the concentration of hydrolyzed silanes in the treatment solution, beneficial results will be obtained over a wide range of silane concentrations and ratios. It is preferred, however, that the solution have at least about 0.1% acyloxy silanes by volume, more preferably at least about 1% acyloxy silanes by volume, most preferably between about 2% and about 5% by volume. Lower vinyl silane concentrations generally provide less corrosion protection. Higher concentrations of acyloxy silanes (greater than about 10%) should also be avoided for economic reasons, and to avoid silane condensation (which may limit storage stability).

The concentration of the basic compound required in the treatment solution varies strongly with the type of acyloxy silane employed and the type of basic compound. Obviously, a strongly acidic solution produced by a highly acyloxy group-substituted acyloxy silane will require an appropriate amount of basic compound to result in a treatment solution with a pH in the pre-determined range. Once the pH of the acyloxy silane in solution is known, an appropriate amount of a basic compound (with a known pH value in solution) can be added to the solution. The relative acidity and basicity of the acyloxy silane and the basic compound may be established before the solution is made up and are commonly presented in standard tables reciting physical properties of known compounds. However, the concentration of the basic compound is generally in the range of about 0.1% and about 10% by volume.

Where a basic silane is used as the basic compound, the solution should have at least about 0.1% basic silanes by volume, more preferably at least about 1% basic silane by volume, more preferably between about 2% and about 10%, most preferably between about 2% and about 5% by volume.

5 As for the ratio of acyloxy silanes to basic compound, a wide range of ratios may be employed, and the present invention is not limited to any particular range of silane ratios.

 The mixture of the acyloxy and basic compound may be provided to the user in a pre-mixed, unhydrolysed form which improves shelf life as
10 condensation of the silane is limited. Such a mixture can then be made up into a treatment solution as defined herein. Such a pre-mixed, unhydrolysed compositions should preferably be substantially free of water but may include one or more organic solvents (such as alcohols). The composition may also include other components such as stabilizers, pigments, desiccants, and the like.

15 Such a pre-mixed composition can be made up with a pre-determined amount of acyloxy silane and basic compound so that the addition of the mixture to water results in a pH within the preferred range. Such pre-mixing prevents or limits a drop in pH, due to the acyloxy silane alone being present in solution, to levels which promote condensation of the silanes in solution. However, the
20 composition can be presented in a "two-pack" kit, wherein one part of the kit comprises the acyloxy silane, while another part of the kit provides the basic compound.

 In either of the above presentation embodiments, the acyloxy silane and basic compound, along with the other components of the composition are
25 provided in a concentrated form as a powder or liquid mixture. In either case, the concentrate is substantially free of water and may be presented in a hermetically sealed container or kit. Preferably, substantially no organic solvent is present in the composition.

 The concentration of the acyloxy silane and basic compound in the pre-
30 mixed concentrate composition is generally in the range 10-100%, preferably 15-80%, most preferably 25-70%. The concentrate may contain numerous

additional components such as stabilisers, pigments, anti-oxidants, basic pH adjusters, desiccants, adhesion promoters, corrosion inhibitors and the like.

The treatment method itself is very simple. Where the solution is to be made up of separately presented components, the unhydrolyzed acyloxy silane, water, basic compound, solvent (if desired), are combined with one another. The solution is then stirred at room temperature in order to hydrolyze the silanes. The solution generally goes clear when hydrolysis is complete. In this embodiment it is beneficial to maintain the pH of the solution above 2 to limit any condensation of the silanes in solution, particularly the acyloxy silanes.

Where the composition is presented as a pre-mixed kit, the composition is simply added to a pre-determined amount of water and mixed until the solution is substantially clear.

The metal surface to be coated with the solution of the present invention may be solvent and/or alkaline cleaned by techniques well-known to those skilled in the art prior to application of the treatment solution of the present invention. The silane solution is then applied to the metal surface (i.e., the sheet is coated with the silane solution) by, for example, dipping the metal into the solution (also referred to as "rinsing"), spraying the solution onto the surface of the metal, or even brushing or wiping the solution onto the metal surface. Various other application techniques well-known to those skilled in the art may also be used. When the preferred application method of dipping is employed, the duration of dipping is not critical, as it generally does not significantly affect the resulting film thickness. It is merely preferred that whatever application method is used, the contact time should be sufficient to ensure complete coating of the metal. For most methods of application, a contact time of at least about 2 seconds, and more preferably at least about 5 seconds, will help to ensure complete coating of the metal.

As the treatment solution is used up, the acyloxy silane concentration is reduced and the acetic acid concentration remains approximately constant as long as no further acyloxy silane is added to the solution. As further acyloxy silane is added to maintain their concentration, acetic acid is built up in the

solution. To maintain the pH in the preferred range pH adjusters may be added such as basic compounds as hereinbefore described, buffers and the like. In one embodiment, a basic compound may be added along with the additional acyloxy silane which forms a salt with the acid in solution. This may form an insoluble salt which can be removed from the process.

The treatment solution may also be heated when applying the treatment solution. Where the treatment solution is heated, the temperature of the treatment solution is generally in the range 20°C to 80°C, preferably 30°C to 50°C.

After coating with the treatment solution of the present invention, the metal sheet may be air-dried at room temperature, or, more preferably, placed into an oven for heat drying. Preferable heated drying conditions include temperatures between about 20°C and about 200 °C with drying times of between about 30 seconds and about 60 minutes (higher temperatures allow for shorter drying times) More preferably, heated drying is performed at a temperature of at least about 90°C, for a time sufficient to allow the silane coating to dry. While heated drying is not necessary to achieve satisfactory results, it will reduce the drying time thereby lessening the likelihood of the formation of white rust during drying. Once dried, the treated metal may be shipped to an end-user, or stored for later use.

The examples below demonstrate some of the superior and unexpected results obtained by employing the methods of the present invention.

Examples

Example 1

Salt Spray test (SST)(Lakebluff) was carried out on A1170/Vinyltriacetoxysilane (1/1, 5%, natural pH=4) treated AA5005 panels. Alkaline cleaned blank and chromated AA5005 panels were chosen as controls. The treated panels were cured at 100°C for 10 min, and then exposed to SST for 29 days, along with the control panels. Four replicates were made for each treatment. The results are presented in Fig. 1.

1. A1170/VTAS treated panels showed original surface after 29 days of exposure to SST, i.e. no corrosion occurred during testing.
2. The blank panels corroded heavily, while the chromated ones pitted apparently.

5 **Example 2**

Salt Spray test (Lakebluff) was carried out on A1170/VTAS (1.5/1.5%, natural pH=4) treated A12024-T3 panels. Alkaline cleaned blank and chromated A12024-T3 panels were chosen as controls. The treated panels were cured at 100°C for 10 min, and then exposed to SST for 7 days, along with the control panels. Three replicates were made for each treatment. The results are presented in Fig. 2.

3. A1170/VTAS treated panels showed almost original surface after 7 days of exposure to SST, i.e., only slight edge corrosion occurred during testing.
4. The blank panels corroded heavily, while the chromated ones pitted slightly.

15 **Example 3**

In order to investigate the paintability of A1170/VTAS water-based silane film on metal substrates, A1170/VTAS (1.5/1.2%, pH=5) water-based silane film was applied on A12023-T3 and HDG, respectively. The treated panels were then powder-painted at Lakebluff with Polyester and Polyurethane powder paints. After that, the panels were put into salt spray chamber for some times, along with the control panels, the blank and the chromated. Three replicates were made for each treatment. The results are shown in Fig. 3.

1. As for A12024-T3 painted with both powder paints (1000hrs in SST), the corrosion performance and paint adhesion improved significantly, which was equal to the chromated and much better than the blank.
2. As for powder-painted HDG (336 hrs in SST), the corrosion performance improved apparently, compared with the chromated

and the blank. The paint adhesion improved somewhat, which was better than the control panels.

Claims

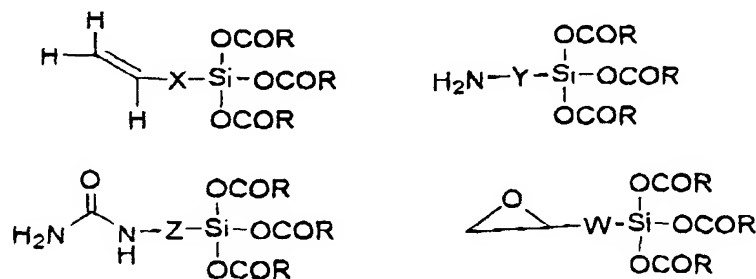
1. A method of treating a metal surface, comprising the steps of:
 - (a) providing a metal substrate; and
 - (b) applying a solution to said metal substrate, said solution comprising
 - (iii) at least one acyloxy silane which comprises at least one acyloxy group, wherein said silane has been at least partially hydrolysed; and
 - (iv) at least one basic compound;

wherein the acyloxy silane and the basic compound are present in concentrations to provide a solution pH of between about 3 and about 10, more preferably between about 4 and about 8, most preferably 4 to 5 and wherein the solution is substantially free of acid other than acid produced upon hydrolysis of the acyloxy silane.
2. The method according to claim 1, wherein the metal surface selected from the group consisting of steel, aluminium, aluminium alloys, zinc, zinc alloys, magnesium, magnesium alloys, copper, copper alloys, tin, and, tin alloys.
3. The method according to claim 1, wherein the metal surface is selected from the group consisting of:
 - a metal surface having a zinc-containing coating;
 - zinc;
 - zinc alloy.
 - Aluminium;
 - Aluminium alloy; and
 - steel.
4. The method according to any preceding claim, wherein the acyloxysilane

comprises a single tetrasubstituted silicon atom, wherein the substituents are individually selected from the group consisting of alkyl, alkenyl, alkynyl, aryl, alkaryl, aralkyl, vinyl, amino, ureido, glycidoxy, epoxy, hydroxy, alkoxy, aryloxy and acyloxy, or any of the group alkyl, alkenyl, alkynyl, aryl, alkaryl and aralkyl substituted by a group selected from the group consisting of vinyl, amine, ureido, glycidoxy, epoxy, hydroxy and alkoxy, with the proviso that at least one of the substituents on the silicon atom is an acyloxy group

5. The method according to any preceding claim, wherein the acyloxy groups are preferably all the same and are selected from the group consisting of C₂₋₁₂ alkanoyloxy, C₃₋₁₂ alkenoyloxy, C₃₋₁₂ alkynoyloxy and C₇₋₁₈ arenoyloxy, preferably C₂₋₆ alkanoyloxy, C₃₋₆ alkenoyloxy, C₃₋₆ alkynoyloxy and C₇₋₁₂ arenoyloxy, preferably ethanoyloxy or methanoyloxy groups.

6. The method according to any preceding claim, wherein the acyloxy silane is selected from the group



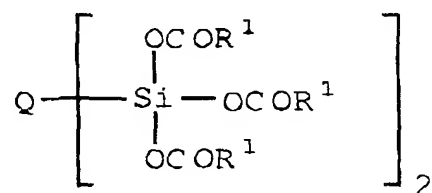
wherein W, X, Y and Z are selected from the group consisting of a C-Si bond, substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups and unsubstituted aromatic groups; and

R is selected from methyl, ethyl and propyl, preferably ethyl.

7. The method according to claim 1, wherein the acyloxy silane comprises more than one silyl group, preferably two silyl groups.

8. The method according to claim 7, wherein the acyloxy groups are the same and are selected from the group consisting of C₂₋₁₂ alkanoyloxy, C₃₋₁₂ alkenoyloxy, C₃₋₁₂ alkynoyloxy and C₇₋₁₈ arenoyloxy, preferably C₂₋₆ alkanoyloxy, C₃₋₆ alkenoyloxy, C₃₋₆ alkynoyloxy and C₇₋₁₂ arenoyloxy, preferably ethanoyloxy and methanoyloxy groups.

9. The method according to claim 7 or 8, wherein the acyloxysilane has the structure



wherein Q is selected from the group consisting of either a bond, an aliphatic or aromatic group; and

R¹ is selected from methyl, ethyl and propyl.

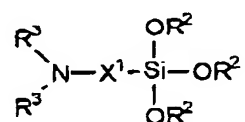
10. The method according to claim 9, wherein Q is selected from the group consisting of a bond, C₁-C₆ alkylene, C₂-C₆ alkenylene, C₁-C₆ alkylene substituted with at least one amino group, C₂-C₆ alkenylene substituted with at least one amino group, C₁-C₆ alkylene substituted with at least one sulfide group containing 1 to 10 sulfur atoms, C₂-C₆ alkenylene substituted with at least one sulfide group containing 1 to 10 sulfur atoms, arylene and alkylarylene

11. The method according to claim 10, wherein the acyloxy silane is selected from the group consisting of bis-(triacetoxysilyl)ethane, bis-(triacetoxysilylpropyl)amine and bis-(triacetoxysilylpropyl)tetrasulfide.

12. The method according to claim 1, wherein the acyloxy silane is vinyltriacetoxysilane.

13. The method according to any preceding claim, wherein the basic compound is selected from the carbonates, hydrogen carbonates and hydroxides of the alkali and alkaline earth metals, organic amines, ammonia, amides and silanes, and mixtures thereof.

14. The method according to any preceding claim, wherein the basic compound is a basic silane compound selected from compounds having the general structure



wherein R^2 is chosen from the group consisting of hydrogen and C_1 - C_{24} alkyl, preferably C_1 - C_6 alkyl and each R may be the same or different;

X^1 is selected from the group consisting of a bond, a substituted or unsubstituted aliphatic or aromatic group; and

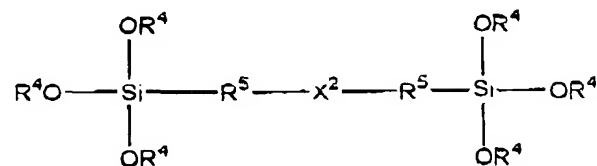
R^3 is a group individually selected from the group consisting of hydrogen, C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_1 - C_6 alkyl substituted with at least one amino group, C_2 - C_6 alkenyl substituted with at least one amino group, arylene and alkylarylene.

15. The method according to claim 14, wherein R^2 is individually chosen from the group consisting of hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl and ter-butyl;

X^1 is selected from the group chosen from the group consisting of a bond, C_1 - C_6 alkylene, C_2 - C_6 alkenylene, C_1 - C_6 alkylene substituted with at least one amino group, C_2 - C_6 alkenylene substituted with at least one amino group, arylene and alkylarylene; and

R^3 is individually selected from the group consisting of hydrogen, ethyl, methyl, propyl, iso-propyl, butyl, iso-butyl, sec-butyl ter-butyl and acetyl.

16 The method of any of claims 1 to 13, wherein the basic compound is a bis-silyl aminosilane(s) having the structure



wherein R^4 is individually selected from the group consisting of: hydrogen and $\text{C}_1 - \text{C}_{24}$ alkyl;

R^5 is individually selected from the group consisting of: substituted aliphatic groups, unsubstituted aliphatic groups, substituted aromatic groups, and unsubstituted aromatic groups; and

$-\text{X}^2$ is either:



wherein each R^6 is individually selected from the group consisting of: hydrogen, substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups; and

R^7 is selected from the group consisting of: substituted and unsubstituted aliphatic groups, and substituted and unsubstituted aromatic groups.

17. The method according to claim 1, wherein the basic compounds are selected from the group consisting of γ -aminopropyltriethoxysilane and γ -aminopropyltrimethoxysilane, *bis*-(trimethoxysilylpropyl)amine, *bis*-(triethoxysilylpropyl)amine and *bis*-(triethoxysilylpropyl)ethylene diamine

18. The method according to any preceding claim, wherein a polymer coating is applied to the treated metal substrate.

19. The method of claim 18, wherein the polymer coating is selected from paints, adhesives, rubbers and plastics.
20. The method according to any preceding claim, wherein the solution contains at least about 0.1% acyloxy silanes by volume, more preferably at least about 1% acyloxy silanes by volume, most preferably between about 2% and about 5% by volume.
21. The method according to any preceding claim, wherein the solution contains at least about 0.1% basic compound by volume, more preferably at least about 1% by volume, more preferably between about 2% and about 10%, most preferably between about 2% and about 5% by volume.
22. A composition comprising an acyloxy silane and a basic compound as defined in any preceding claim, wherein the solution pH is between 3 and about 10, more preferably between about 4 and about 8, most preferably 4 to 5 and wherein the solution is substantially free acids other than acids produced upon hydrolysis of the acyloxy silanes.
23. The composition according to claim 22, wherein the solution contains at least about 0.1% acyloxy silanes by volume, more preferably at least about 1% acyloxy silanes by volume, most preferably between about 2% and about 5% by volume.
24. The composition according to claim 22 or 23, wherein the solution contains at least about 0.1% basic compound by volume, more preferably at least about 1% by volume, more preferably between about 2% and about 10%, most preferably between about 2% and about 5% by volume.

25. A composition comprising an acyloxy silane and a basic compound as defined in any of claims 1 to 22, wherein the acyloxy silane is substantially unhydrolysed and the composition is substantially free of water.

26. The composition according to claim 25, wherein the combined concentration of the acyloxy silane and basic compound in composition is generally in the range 10-100%, preferably 15-80%, most preferably 25-70%.

27. The composition according to claim 26, wherein the concentrations of acyloxy silane and basic compound pre-determined so as to provide a solution with a pH in the range of between 3 and about 10, more preferably between about 4 and about 8, most preferably 4 to 5 when dissolved in water.

28. The composition according to any of claims 22 to 27, comprising additional components selected from stabilisers, pigments, anti-oxidants, desiccants, adhesion promoters, corrosion inhibitors and mixtures thereof.

29. A kit comprising a composition according to any of claims 22 to 28.

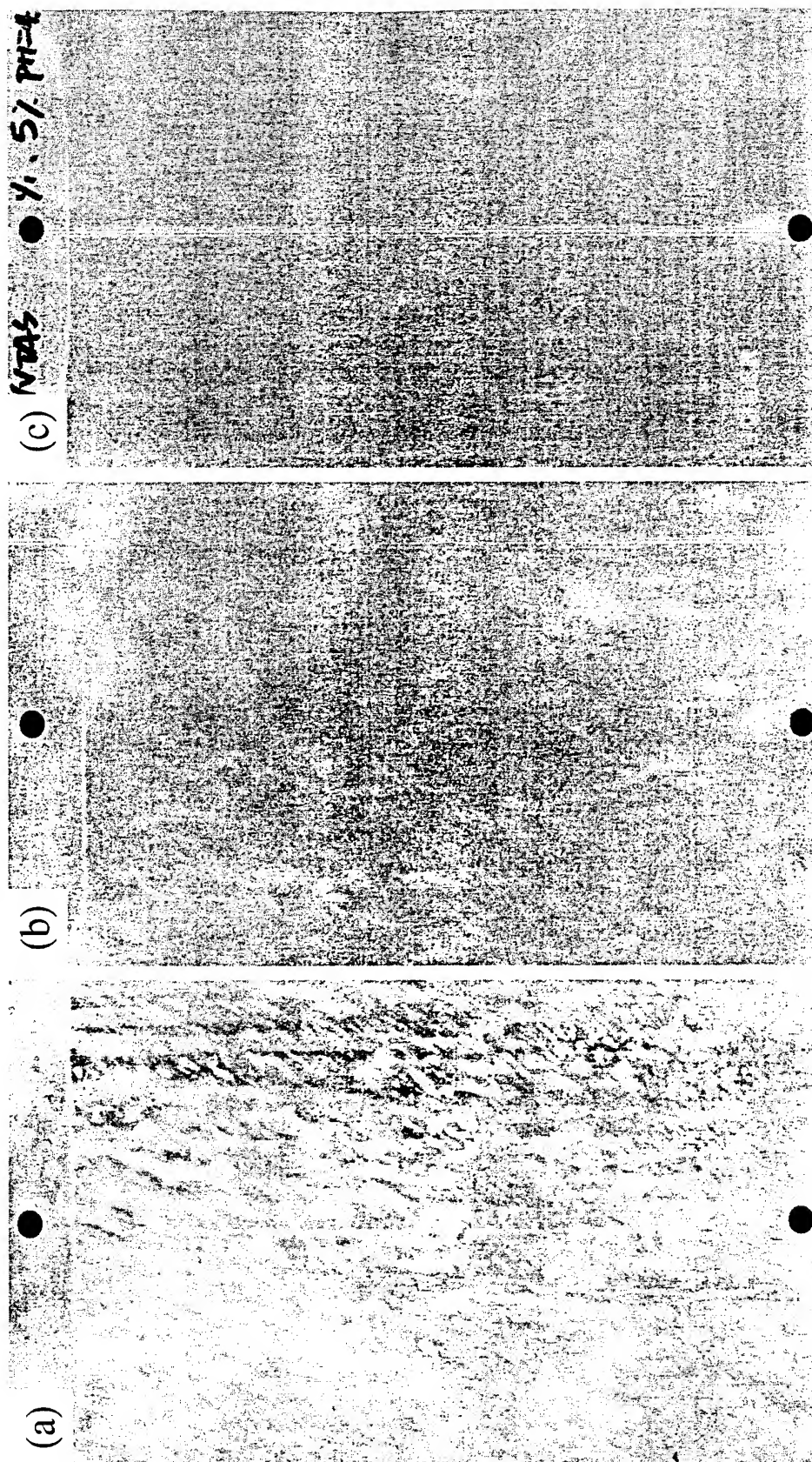


Fig.1. A1170/VTAS Mix. Treated AA5005 after 29 days of SST

(a) Blank; (b) Chromamted; (c) A1170/VTAS treated*

* A1170/VTAS: 1.5/1, natural pH=4

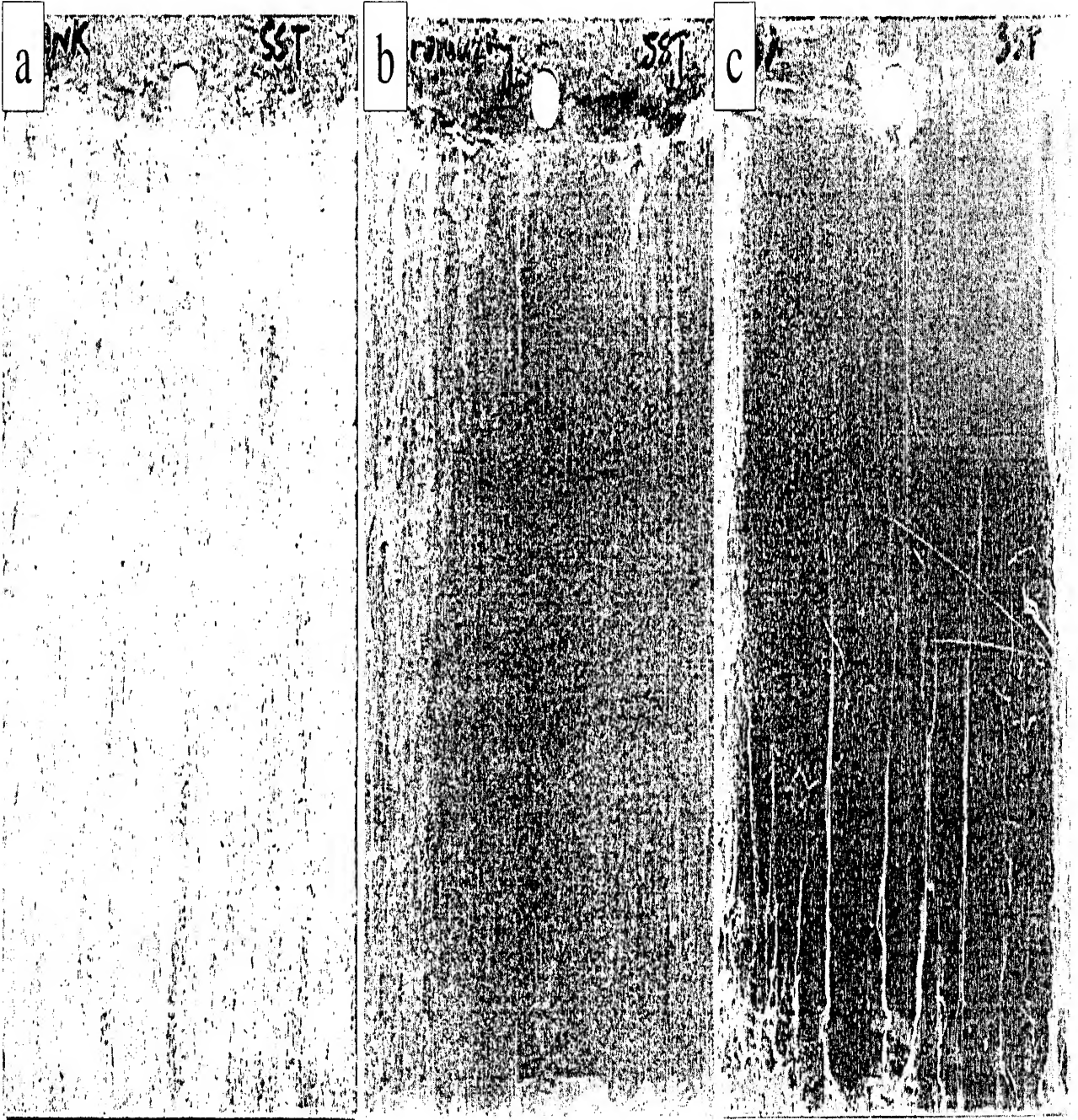


Fig. 2. A1170/VTAS Mix. treated Al2024-T3 after 7days of SST
(a) Blank; (b) Chromated; (c) A1170/VTAS treated
* A1170/VTAS: 1.5/1, 5%, natural pH=4

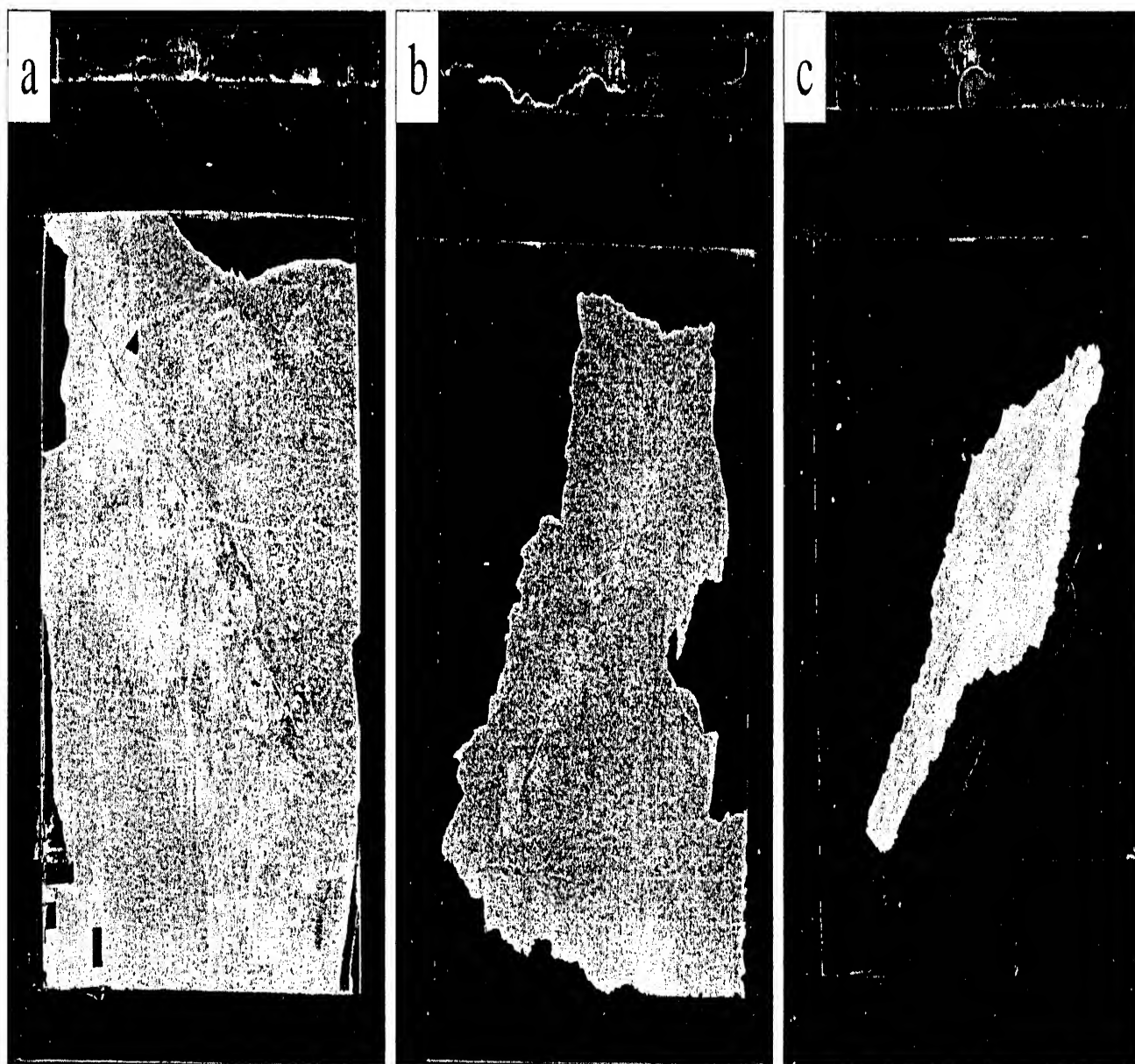


Fig. 3a Polyester powder painted HDG after 336 hrs of SST

(a) Blank; (b) Chromated; (c) A1170/VTAS treated

* A1170/VTAS: 1.5/1, 2%, natural pH=5

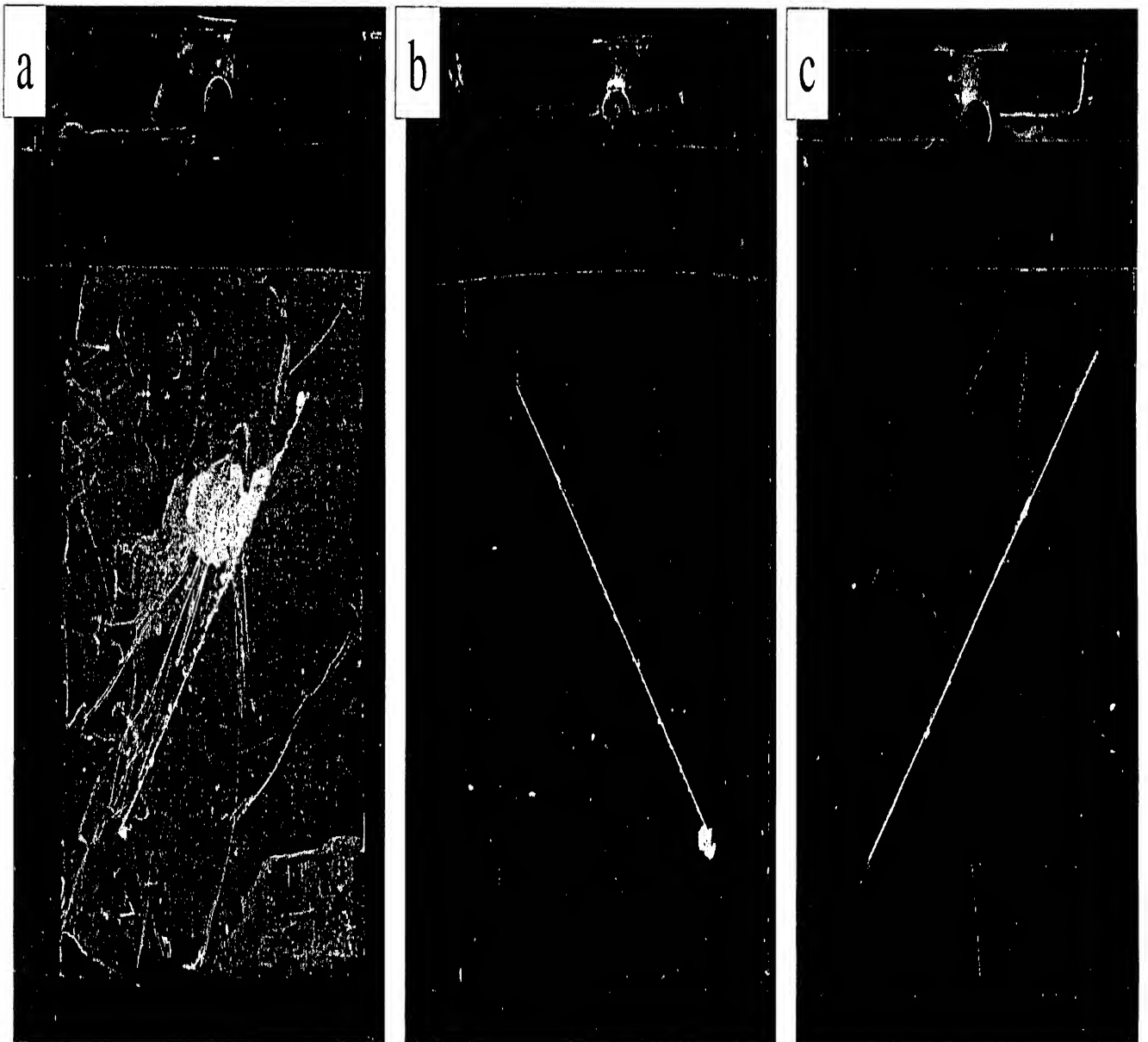


Fig. 3b. Polyester powder painted Al2024-T3 after 1000 hrs of SST
(a) Blank; (b) Chromated; (c) A1170/VTAS treated

* A1170/VTAS: 1.5/1, 2%, natural pH=5

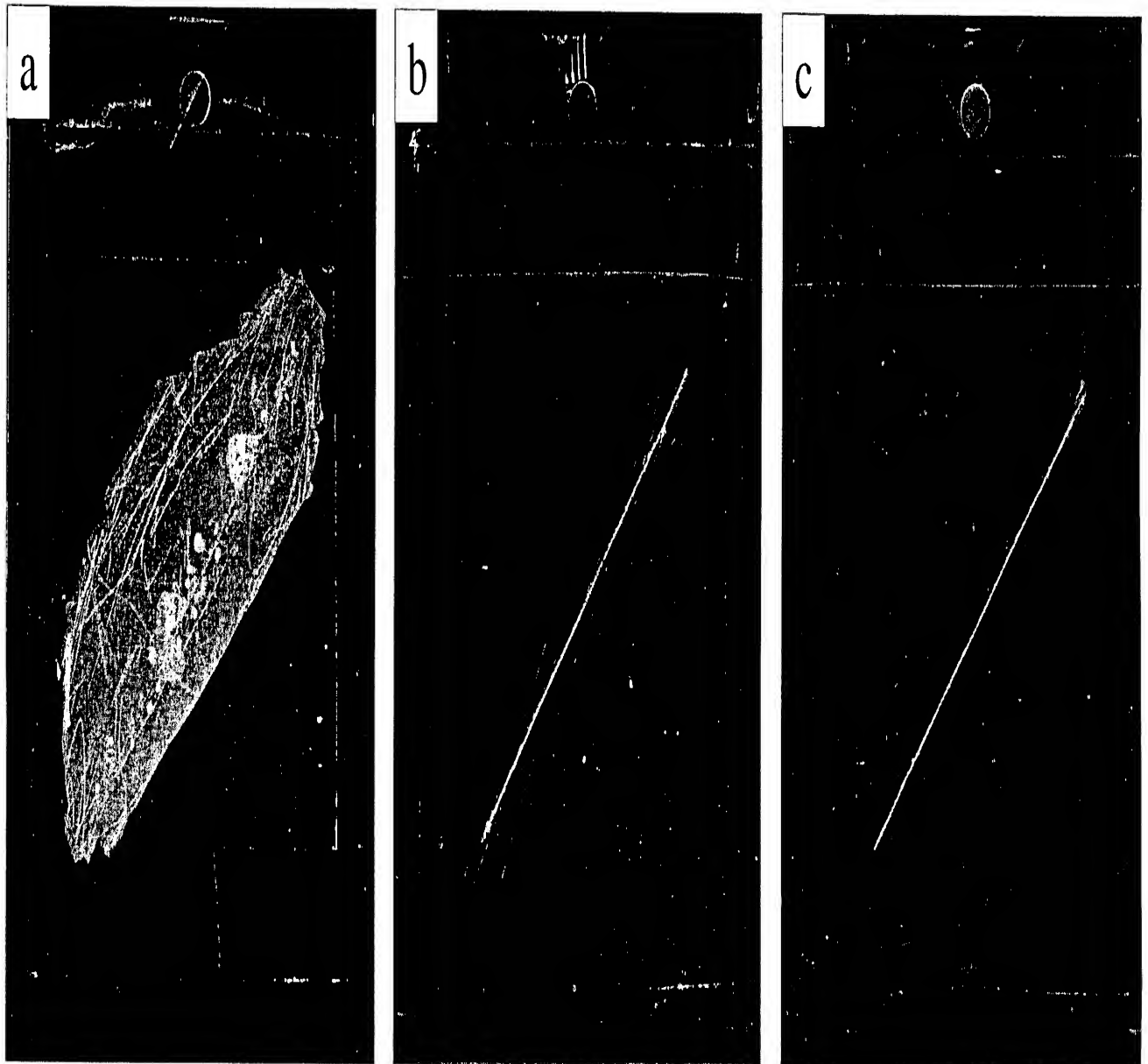


Fig. 3c Polyurethane powder painted Al2024 after 1000 hrs of SST
(a) Blank; (b) Chromated; (c) A1170/VTAS treated

* A1170/VTAS: 1.5/1, 2%, natural pH=5

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/19646

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C22/56 C23C22/53 C23C22/48 C23C22/68 C23C22/60

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 20705 A (AAR CORNELIS P J V D ;OOIJ WIM J VAN (US)) 29 April 1999 (1999-04-29) claims 1,9,13-16	1-29
A	WO 98 19798 A (OOIJ WIM J VAN ;UNIV CINCINNATI (US); YUAN WEI (US)) 14 May 1998 (1998-05-14) claims 1-15	1-5
A	US 5 750 197 A (SUBRAMANIAN VIJAY ET AL) 12 May 1998 (1998-05-12) claims 1-15	1-5



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

31 October 2000

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/19646

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9920705 A	29-04-1999	AU 1198799 A EP 1032616 A	10-05-1999 06-09-2000
WO 9819798 A	14-05-1998	US 5759629 A AU 724454 B AU 5479198 A BR 9712744 A CN 1239908 A EP 0959990 A PL 333326 A ZA 9709948 A	02-06-1998 21-09-2000 29-05-1998 21-12-1999 29-12-1999 01-12-1999 06-12-1999 05-11-1998
US 5750197 A	12-05-1998	AU 5862498 A BR 9807057 A WO 9830735 A EP 1015662 A PL 334657 A ZA 9800133 A	03-08-1998 02-05-2000 16-07-1998 05-07-2000 13-03-2000 08-01-1999